

X-ray reflectivity study of formation of multilayer porous anodic oxides of silicon

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Introduction

While polarizing silicon wafers galvanostatically in strong inorganic acids at increased temperatures, one can observe very the interesting phenomenon of oscillating kinetics of the anodic potential. To date, it is not known what happens structurally during the oscillatory changes. Using *in situ* x-ray reflectivity measurements, we demonstrate that dense/sparse oxide strata are formed during the potential oscillations.

Methods and Materials

Single crystals of commercially polished silicon were anodically oxidized in 1.0 M H_3PO_4 electrolytes. An unfocused monochromatic beam of x-rays with energy of 16 keV was used. At this energy, attenuation of x-rays through 10 millimeters of solution is $\sim 30\%$, permitting *in situ* examination.

Results

The voltage oscillation during galvanostatic oxidation of the silicon (100) surface is shown in Figure 1. The oscillations are very regular at low current densities and in concentrated electrolytes. Figure 2 shows the x-ray reflectivity curves taken *ex situ* from four samples grown at the same current (0.5 mA) and corresponding to the different stages of the oscillatory kinetics (these stages are specified in Figure 1 by arrows). All curves show well-defined intensity oscillations suggesting the presence of surface film.

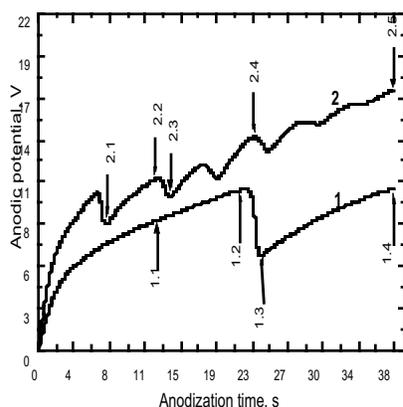


Figure 1: Kinetics of p-Si anodization in 1.0 M H_3PO_4 at 50 °C and current density of 0.5 mA/cm² (curve 1) and 2 mA/cm² (curve 2). The arrows mark the moments when the anodization process was stopped to obtain the samples 1.1–1.4 and 2.1–2.5.

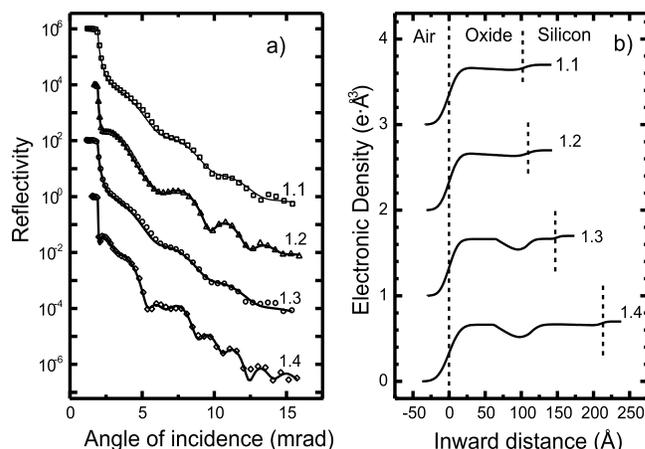


Figure 2: Reflectivity scans from samples 1.1–1.4. a) Corresponding electronic density profiles, and b) the experimental points rarefied three times to make fit curves visible.

The samples 1.1–1.3, which correspond to the first period of the anodic potential oscillations, show simple oscillatory amplitude of the reflected beam. This is a result of interference of x-rays reflected mainly from top and bottom interfaces of a uniform oxide film [1].

Discussion

The sample 1.4 shows the oscillations with more complex amplitudes. In addition to the main (or envelope) oscillation seen in first three samples, another one with the period nearly half of the main oscillation appears in the reflectivity curve. Even without performing fitting of the reflectivity curves, one can recognize a double-layer structure of the oxide in the sample 1.4 that corresponds to the maximum of second oscillation of the anodic voltage. The samples treated at 2 mA (curve 2 in Figure 1) also show this dependence between the number of oscillations of anodic potential and a number of suboscillations in the reflectivity curves (not shown). The number of suboscillations within the main “envelope” oscillation is exactly equal to the number of voltage oscillations during the treatment.

We have thus established the rather impressive fact that the number of the suboscillations in envelope oscillation is equal to the number of maxima of anodic potential observed during the oxide growth. This finding presents clear-cut evidence of the multilayered structure of the growing oxide film.

What is interesting to note here is that although the sample 1.2 corresponds to an anodization time twice as large as that corresponding to 1.1, its thickness is only slightly higher. This means that while the anodic potential saturates, the efficiency of the oxide growth is decreased (some side reactions not associated with the oxide growth become increasingly important).

The sample 1.3 (corresponding to the moment of the first drop of the anodic voltage, see Figure 1) shows essentially thicker overall oxide thickness—about 140 Å—showing that there is an intensive thickening of the oxide at the time interval marked by the arrows 1.2 and 1.3. Density distribution experiences an essential change. At the depth of 100 Å from the surface there is a large density minimum, probably associated with the formation of large pores. They occupy about 20% of the oxide volume. This region of increased porosity separates two oxide layers of higher density, each with the properties similar to those of the sample 1.1 and 1.2.

Acknowledgments

The experiment was performed at 12-BM-B, the Advanced Photon Source (APS). The use of APS was supported by the U.S. Department of Energy (DOE), Basic Energy Sciences (BES), Office of Science, under Contract No. W-31-109-Eng-38. This work was supported by Materials Science Program of DOE, BES.

Reference

- [1] V. Parkhutik, Y. Chu, H. You, Z. Nagy, and P.A. Montano, *J. of Porous Materials* **7**, 27–31 (2000).